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**SYNTHESIS OF DUAL NIR TWO-PHOTON
ABSORPTIVE [60]FULLERENYL MULTIADDUCTS FOR
NONLINEAR LIGHT-TRANSMITTANCE REDUCTION
APPLICATION (POSTPRINT)**

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Interim Report**

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Synthesis of dual NIR two-photon absorptive [60]fullerenyl multiadducts for nonlinear light-transmittance reduction application

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ABSTRACT

Synthesis of several C_{60} -(antenna)_x conjugates was performed to demonstrate high flexibility in the design of organic nonlinear optical (NLO) nanostructures showing broadband characteristics with capability to absorb light over a wide range of wavelengths. It was achieved by covalent attachment of a hybrid combination of two types of light-harvesting fluorescent antenna chromophores on a C_{60} cage. Ultrafast photoresponsive intramolecular Förster resonance energy-transfer among antenna units and shared excited energy-accepting C_{60} cage is proposed as a plausible mechanism to enhance the broadband NLO ability. Characterization of the branched triad $C_{60}(>DPAF-C_{18})(>CPAF-C_{2M})$ and the tetrad $C_{60}(>DPAF-C_{18})(>CPAF-C_{2M})_2$ was carried out by various spectroscopic techniques. These compounds showed approximately equal extinction coefficients of optical absorption over 400–550 nm that corresponds to near-IR two-photon based excitation wavelengths at 780–1100 nm. These nanomaterials may be utilized in NLO coatings for achieving efficient light-transmittance reduction at the same NIR wavelengths.

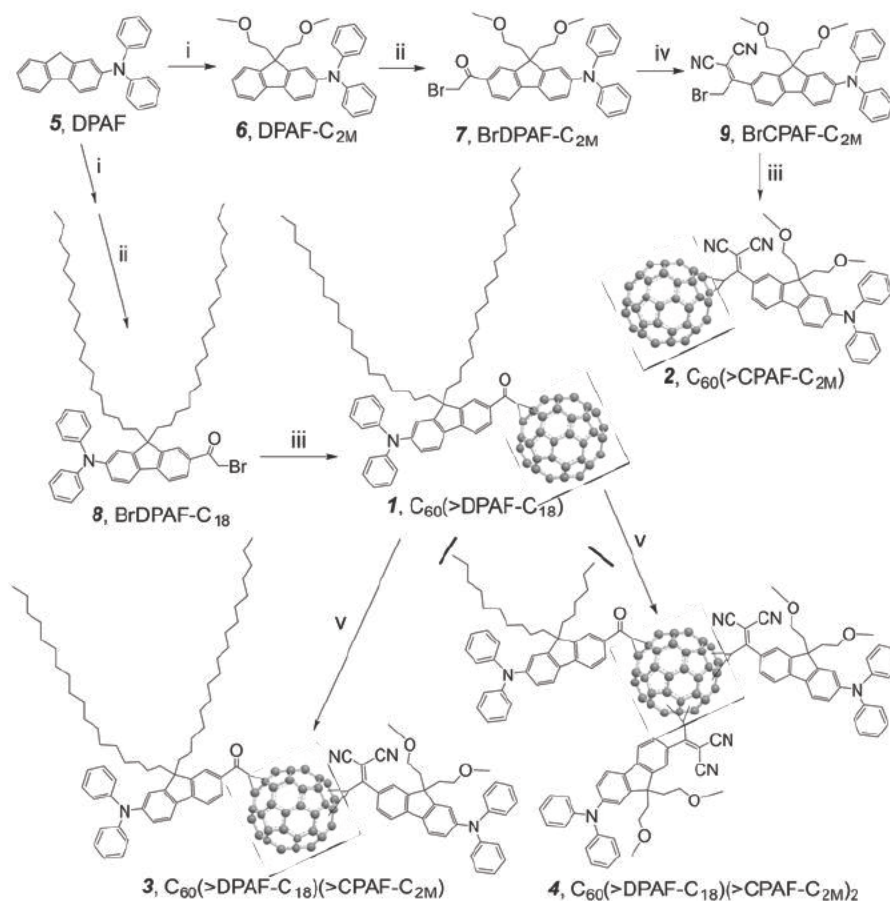
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1. INTRODUCTION

Nonlinear optical characteristics of [60]fullerene-derived C_{60} -(antenna)_x nanostructure conjugates are based on excited singlet state-based reverse saturable absorption (RSA) [1,2] events of both the C_{60} cage and antenna units in the combined wide UV-visible–NIR region and effective two-photon absorption (2PA) processes in the NIR region [3]. Fullerene cages exhibit high electronegativity and electron-accepting characteristics. Base-induced nucleophilic additions of one or more stable light-harvesting electron-donating antenna chromophores forming the corresponding C_{60} -(antenna)_x conjugates make them effectively photoinducible donor-acceptor pairs in the structure capable of undergoing various electron- and energy-related photophysical processes [4,5]. Well-controlled chemical modification of C_{60} by only one to three functionalized sites (or fulvalenyl double bonds) leads to derivatives without much change of their cage redox properties. Conversely, attachment of multiple light-harvesting fluorescent antenna units to a C_{60} cage largely enhances visible to NIR absorption extinction coefficient values of resulting derivatives that provides remedy to low absorption of C_{60} in this wavelength range. We have recently demonstrated the use of multiple highly photostable and fluorescent 7-acetyl-9,9-dialkyldiphenylaminofluorenes (DPAF- C_n) as antenna units to increase 2PA cross-sections of the products $C_{60}(>DPAF-C_n)_x$ in NIR wavelengths [6,7,8]. The absorbed photoenergy by the donor DPAF- C_n antenna was able to undergo efficient intramolecular electron- or energy-transfer to the fullerene acceptor moiety in femtoseconds [8], leading to the generation of $^1(C_{60}>)^*$. Triplet energy transfer from excited triplet cage state $^3(C_{60}>)^*$ to molecular oxygen produces singlet oxygen (1O_2) after intersystem crossing from $^1(C_{60}>)^*$ that gives the cytotoxic effect to the pathogenic cells via the Type-II photochemistry [9-12]. Meanwhile, their appreciably high concentration-dependent 2PA cross-section values at 800 nm transform these nanomaterials to efficient nonlinear optical absorbers suitable for applications showing light-transmittance reduction in intensity at NIR wavelengths.

Here, we report the synthesis and spectroscopic characterization of several photoresponsive two-photon absorptive [60]fullerene dyads, triads, and tetrads associated with two types of light-harvesting donor antenna, DPAF- C_{18} and 1-

(1,1-dicyanoethylenyl)-1-methyl]-9,9-di(2-dimethoxyethyl)-2-diphenylamino fluorene CPAF- C_{2M} , showing linear absorption maximum (λ_{max}) centered at 417 and 500 nm, respectively. They were synthesized using the corresponding structurally well-characterized [60]fullerene monoadduct precursors, $C_{60}(>>\text{DPAF}-C_{18})$ **1** and $C_{60}(>>\text{CPAF}-C_{2M})$ **2**, to construct the multiadduct nanostructures, as shown in Scheme 1. The resulting triads **3** and tetrads **4** were found to be capable of performing two-photon absorption-based photoexcitation processes at either 780 or 980 nm to reduce the light intensity in transmission.



Scheme 1. Synthetic procedures for the preparation of C_{60} -(antenna) $_x$ triad $C_{60}(>>\text{DPAF}-C_{18})(>>\text{CPAF}-C_{2M})$ **3** and tetrad $C_{60}(>>\text{DPAF}-C_{18})(>>\text{CPAF}-C_{2M})_2$ **4**. Reagent and reaction conditions: i. 2-MeOCH₂CH₂-OMs (for **6**), 1-C₁₈H₃₇Br (for **8**), *t*-BuOK in THF, 0 °C–r.t., 4 h; ii. bromoacetyl bromide, AlCl₃, ClCH₂CH₂Cl, 0 °C, 4 h; iii. C_{60} , DBU, toluene, r.t., 4 h; iv. TiCl₄, pyridine, CH₂(CN)₂, CHCl₃, r.t., 5.0 min; v. DBU, toluene, r.t., 4 h.

2. EXPERIMENTAL SECTION

2.1 Materials

Reagents of 1,8-diazabicyclo[5,4,0]-undec-7-ene (DBU), 1-bromooctadecane, 2-bromofluorene, sodium *t*-butoxide, potassium *t*-butoxide, aluminum chloride, titanium chloride, and 2-methoxy-ethanol, were purchased from Aldrich Chemicals. Reagent of 1-bromooctadecane was purchased from Tokyo Chemical Industry Co., Ltd. C_{60} samples with a purity of 99.0% was purchased from Term USA, Inc.

2.2 Synthetic Procedures

2.2.1 Synthesis of 7- α -bromoacetyl-9,9-di(2-methoxyethyl)-2-diphenylaminofluorene, BrDPAF-C_{2M} (**7**), 7- α -bromoacetyl-9,9-dioctadecyl-2-diphenylaminofluorene, BrDPAF-C₁₈ (**8**), and 7-[2-bromo-1-(1,1-dicyanoethylenyl)-1-methyl]-9,9-di(2-dimethoxyethyl)-2-diphenylaminofluorene, BrCPAF-C_{2M} (**9**)

Preparation methods of the intermediate compounds **7**, **8**, and **9** follow the modified procedures reported previously [13].

2.2.2 Synthesis of 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-dioctadecyl-2-diphenylaminofluorene, C₆₀(>DPAF-C₁₈) (**1**) and 7-(1,2-dihydro-1,2-methano[60]fullerene-61-{1,1-dicyanoethylenyl})-9,9-di(2-methoxyethyl)-2-diphenylaminofluorene, C₆₀(>CPAF-C_{2M}) (**2**)

Preparation methods of the [60]fullerenyl monoadducts **1** and **2** follow the modified procedures reported previously [13].

2.2.3 Synthesis of hybrid [(9,9-dioctadecyl-2-diphenylaminofluorenyl)-7-carbonyl]-{[9,9-(2-dimethoxyethyl)-2-diphenylaminofluorenyl]-7-(1,1-dicyanoethylenyl)}-bis(1,2-dihydro-1,2-methano[60]fullerenyl triad C₆₀(>DPAF-C₁₈)(>CPAF-C_{2M}) (**3**) and its tetrad analog C₆₀(>DPAF-C₁₈)(>CPAF-C_{2M})₂ (**4**)

To the mixture of 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-di(octadecyl)-2-diphenylaminofluorene C₆₀(>DPAF-C₁₈) **1** (0.48 g, 0.3 mmol) and 7-[2-bromo-1-(1,1-dicyanoethylenyl)-1-methyl]-9,9-di(2-methoxyethyl)-2-diphenylaminofluorene **9** (BrCPAF-C_{2M}, 0.37 g, 0.6 mmol) in dry toluene (100 mL) was added 1,8-diazabicyclo[5,4,0]-undec-7-ene (DBU, 0.1 M, 6.0 mL) slowly under a nitrogen atmosphere. After stirring at room temperature for a period of 5.0 h, the reaction mixture was concentrated to a volume of approximately 10 mL. Crude product was precipitated by the addition of methanol and isolated by centrifugation (8000 rpm, 20 min). The isolated solid was found to be a mixture of the fullerene multiadducts. Separation of these mixture was made by column chromatography (silica gel) using a solvent mixture of toluene–ethyl acetate (9:1) as the eluent. The first chromatographic band gave the unreacted starting compound **1** (0.08 g, 0.05 mmol). The second chromatographic band corresponding to $R_f = 0.5$ on the thin-layer chromatographic plate [TLC, SiO₂, toluene–ethyl acetate (9:1) as the eluent] afforded the bisadduct product C₆₀(>DPAF-C₁₈)(>CPAF-C_{2M}) **3** as orange-brown solids (0.15 g, 0.07 mmol) in a 28% yield [based on the recovered C₆₀(>DPAF-C₁₈) amount]. The third chromatographic band corresponding to $R_f = 0.4$ on the thin-layer chromatographic plate [TLC, SiO₂, toluene–ethyl acetate (4:1) as the eluent] afforded the trisadduct product C₆₀(>DPAF-C₁₈)(>CPAF-C_{2M})₂ **4** as red-brown solids (0.28 g, 0.10 mmol) in a yield of 40% [based on the recovered C₆₀(>DPAF-C₁₈) amount]. Spectroscopic data of **3** and **4** were given in the recent report [13].

2.3 Spectroscopic Measurements

Infrared spectra were recorded as KBr pellets on a Thermo Nicolet Avatar 370 FT-IR spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance Spectrospin-500 spectrometer. UV-vis spectra were recorded on a Perkin Elmer Lambda 750 UV-vis-NIR Spectrometer. Mass spectroscopic measurements were performed by the use of positive ion matrix-assisted laser desorption ionization (MALDI-TOF) technique on a micromass M@LDI-LR mass spectrometer. The sample blended or dissolved in the matrix material was irradiated by nitrogen UV laser at 337 nm with 10 Hz pulses under high vacuum. Mass ion peaks were identified for the spectrum using the MassLynx v4.0 software. In a typical experiment, the samples of C₆₀(>DPAF-C₁₈), C₆₀(>CPAF-C_{2M}), C₆₀(>DPAF-C₁₈)(>CPAF-C_{2M}), or C₆₀(>DPAF-C₁₈)(>CPAF-C_{2M})₂ were dissolved in CHCl₃ in a concentration of 1.0 mg/mL. The matrix of 3,5-dimethoxy-4-hydroxycinnamic acid (sinapic acid) was dissolved in THF in a concentration of 10 mg/mL. The solution of matrix (1.0 mL) was taken and mixed with the sample solution (0.1 mL) prior to the deposition on a stainless-steel MALDI target probe. It was subsequently dried at ambient temperature.

2.4 Z-scan and Light-Intensity-Dependent Transmittance Measurements

Z-scan measurements and irradiance-dependent transmission measurements were carried out at the wavelength of either 780 or 980 nm using 125-fs laser pulses with the repetition rate of 1.0 kHz. Laser pulses were generated by an optical parametric amplifier system (TOPAS) pumped by a Ti:Sapphire regenerative amplifier (Spitfire Pro, Spectra Physics/Newport) and focused onto a 1.0-mm thick quartz cuvette containing a solution of methano[60]fullerene derivatives. Incident and transmitted laser intensities were monitored as the cuvette was moved (or Z-scanned) along the propagation direction of the laser pulses. The data sets were normalized to the linear transmittance and sample inhomogeneities for all Z-scans by the correction of the background transmittance, $T(|Z| - Z_0)$. Total absorption was described by the change in the absorption coefficient $\Delta\alpha = \beta I$, where β and I are the 2PA coefficient and the light intensity, respectively. The absorption coefficient could be extracted from the line fitting between the Z-scan theory and the data. The 2PA cross-section value was then calculated from the coefficient by the formula $\sigma_2 = \beta\hbar\omega/N$, where $\hbar\omega$ is the photon energy and N is the number of the molecules.

3. RESULTS AND DISCUSSION

3.1 Design and Preparation of Hybrid [60]Fullerene Triads and Tetrads

Covalent attachment of combined highly fluorescent chromophores of 7-acetyl-9,9-dioctadecyl-2-diphenylaminofluorene DPAF-C₁₈ (λ_{max} 410 nm) and 1-(1,1-dicyanoethylenyl)-1-methyl]-9,9-di(2-dimethoxyethyl)-2-diphenylaminofluorene CPAF-C_{2M} (λ_{max} 503 nm) antenna moieties as hybrid addends to a single C₆₀ cage should result in the formation of corresponding fullereryl multiadducts capable of facilitating dual-band or broadband NLO characteristics upon high-power radiation at both 800 and 1000 nm. The structural design of hybrid [60]fullerene triads and tetrads was based on both linear and nonlinear optical characteristics of the precursor monoadducts C₆₀(>DPAF-C₁₈) **1** [14] and C₆₀(>CPAF-C_{2M}) **2** [11], to construct an unique nanostructure system with a shared C₆₀ cage, as shown in Scheme 1. The linkers used for connecting a C₆₀ and donor antenna chromophore moieties are either cyclopropenylketo or cyclopropenyl-1,1-dicyanoethylenyl groups, respectively, in a functional periconjugation arrangement to achieve a configuration with a physical separation distance of only <3.5 Å between the donor antenna and C₆₀ acceptor moieties. This led to the realization of ultrafast intramolecular energy- and/or electron-transfer from photoexcited antenna moiety to C₆₀ in <130–150 fs [8] that made the corresponding C₆₀-antenna conjugates, C₆₀(>DPAF-C_n)_x, capable of exhibiting photoresponse in a nearly instantaneous time scale to protect against high-intensity radiation. By increasing the number of attached antennae to four per C₆₀ cage giving starburst pentad nanostructures, highly enhanced fs 2PA cross-section values (~8000 GM) were observed in a concentration-dependent manner [15]. Flexibility in chemical modification between the keto and 1,1-dicyanoethylenyl (DCE) groups was demonstrated to extend the π -conjugation, to increase the molecular electron push–pull polarization, and to cause a large bathochromic shift of the linear optical absorption in nearly 100 nm. The shift considerably increased its light-harvesting ability in visible to NIR wavelengths as compared with those of the parent C₆₀.

Synthetically, the relatively large bulkiness of DPAF-C₁₈ and CPAF-C_{2M} in sizes and, physically, in close vicinity to C₆₀ can prevent any of these two types of antenna moieties from positioning themselves tightly to each other on the cage surface. By considering the regio-location of reactive bicyclopentadienyl olefin bonds on the fullerene surface, when the first antenna is bound at the north-pole location, the second antenna arm is most likely to be pushed away to the equator area of the C₆₀ sphere. Therefore, only a limited number of multiadduct regioisomers per C₆₀ are likely to be formed. Therefore, we predicted a confined number of isomeric products possible in the synthesis by such structural design. Preparation procedures and methods for fabrication of hybrid methano[60]fullerene triads, C₆₀(>DPAF-C₁₈)(>CPAF-C_{2M}) **3**, and tetrads, C₆₀(>DPAF-C₁₈)(>CPAF-C_{2M})₂ **4**, with their structures were given in Scheme 1. The syntheses were accomplished by the use of a structurally well-defined monoadduct **1** followed by the attachment of one or two CPAF-C_{2M} antenna in sequence. A key intermediate reagent precursor BrDPAF-C₁₈ **8** was prepared by a three-step reaction involving first palladium catalyzed diphenylation of commercially available 2-bromofluorene at the C2 position of the fluorene ring to afford DPAF **5**. It was followed by dialkylation at the C9 carbon position of **5** using 1-bromooctadecane as the reagent in the presence of potassium *t*-butoxide, as a base, in THF at 0–25 °C to give the corresponding DPAF-C₁₈ in 97% yield. Friedel-Crafts acylation of DPAF-C₁₈ with α -bromoacetyl bromide and AlCl₃ in 1,2-dichloroethane at 0 °C for a period of 4.0 h afforded the compound BrDPAF-C₁₈ in a yield of 96%. Addition reaction of **8** to C₆₀ was carried out in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.0 eq.) at ambient temperature for 4.0 h to result in **1** in 65% yield (based on recovered residual C₆₀) after column chromatographic purification. A similar reaction sequence was applied for the synthesis of the monoadduct **2** by replacing two octadecyl groups by 2-methoxyethyl groups. It was obtained as orange red solids in 53% yield (based on recovered C₆₀).

By controlling the reaction kinetic rate and applying only two molar equivalents of CPAF-C_{2M} in the reaction with **1** in the presence of DBU (2.0 eq.), only two clear PTLC (SiO₂, toluene–ethyl acetate/9:1 as the eluent) chromatographic bands arising from the product mixtures were observed in addition to the starting **1** (~15%). The first less polar product band at R_f = 0.5 was found to be the bisadduct **3** isolated as orange-brown solids in 28% yield. The second more polar product band at R_f = 0.4 (toluene–ethyl acetate/4:1 as the eluent) was determined to be the trisadduct **4** isolated as red-brown solids in 40% yield.

3.2 Spectroscopic Characterization of Hybrid [60]Fullerene Triads and Tetrads

We utilized well-characterized structures of **1** and **2** for the correlation of ¹H NMR spectra to hybrid [60]fullerene triads **3** and tetrads **4**. Upon the attachment of one CPAF-C_{2M} antenna arm to **1**, large difference of ¹H chemical shifts among alkyl groups of DPAF-C₁₈ (methyl and the most of methylene proton peaks at δ 0.69–1.29) and CPAF-C_{2M} (singlet terminal methoxy CH₃-O– proton peak at δ 2.95 and triplet methylenoxy –CH₂-O– proton peaks centered at δ 2.73)

allowed us to measure a clear proton integration ratio count to verify the structure of **3** and **4** as a bisadduct and trisadduct, respectively, as shown in Figure 1. A more branched structure of **4** was also evident by the detection of a higher aromatic proton integration ratio in the region of δ 7.5–7.8 and 8.10–8.15 (Figures 1a and 1d) of CPAF moieties. The most distinguishable proton peaks at δ 5.5–5.7 in these spectra were assigned for α -protons each bound on the cyclopropanyl carbon located between either the keto (for DPAF) or DCE (for CPAF) group and the C₆₀ cage. Owing to the fullerenyl ring current, a large down-field shift of the δ value was observed at δ 5.66 (for the keto α -H) and 5.51 (for the DCE α -H) from that of the fluorenyl α -bromoketo α -H at δ 4.61 (Figures 1a and 1b) or δ 2.6 for fluorenyl keto α -H (without α -attachment of a bromine atom, a large shift of \sim 3.0 ppm). It also caused a down-fielded δ shift of 0.44–0.48 ppm for fluorenyl protons located at the vicinity of C₆₀> moiety that clearly revealed strong electronic interactions between DPAF-C₁₈/CPAF-C_{2M} antenna moieties and the fullerene cage. A number of α -H peaks were observed in the ¹H NMR spectrum of **3** (the inset of Figure 1c). By taking the consideration of four possible different orientational configurations for each regioisomer, one regioisomeric molecule may display four keto α -H_a peaks (from the DPAF-C₁₈ moiety) and four DCE α -H_b peaks (from the CPAF-C_{2M} moiety) in the region of δ 5.0–5.75. Therefore, detected α -H_a peaks each in different intensities can be separately grouped into and accounted for two major regioisomer products and one minor regioisomer product. High similarity of molecular polarity among these regioisomers prohibited us to separate them chromatographically.

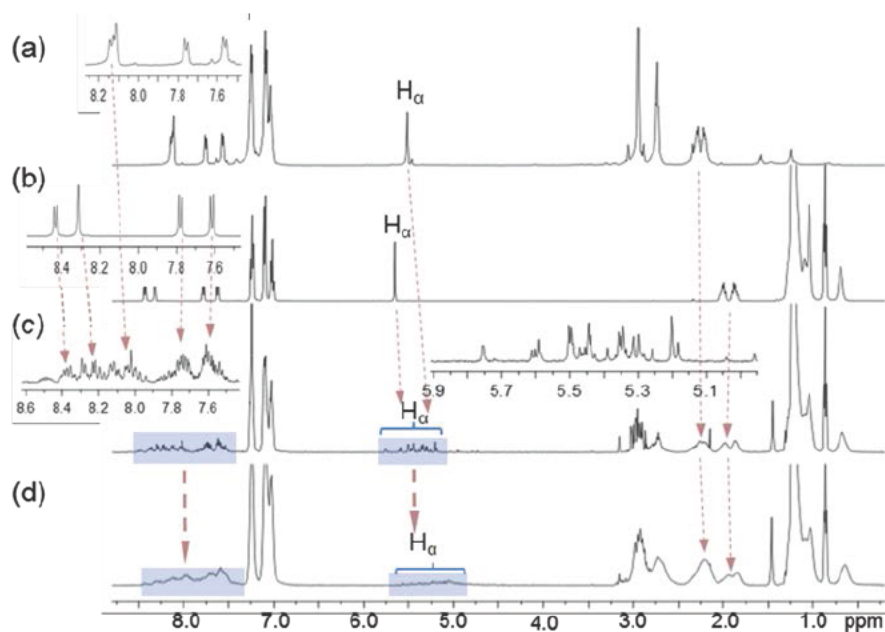


Figure 1. ¹H NMR spectra (CDCl₃) of (a) C₆₀(>CPAF-C_{2M}) **2**, (b) C₆₀(>DPAF-C₁₈) **1**, (c) C₆₀(>DPAF-C₁₈)(>CPAF-C_{2M}) **3**, and (d) C₆₀(>DPAF-C₁₈)(>CPAF-C_{2M})₂ **4**.

Structural identification of C₆₀-(antenna)_x nanostructures was also carried out by using MALDI-TOF mass spectroscopic measurements first with the samples of C₆₀(>CPAF-C_{2M}) **2** (Figure 2a) and C₆₀(>DPAF-C₁₈) **1** (Figure 2b). In the case of multiadducts, we were able to confirm the identical composition mass of several regioisomer fractions (TLC) of **3** by detecting a group of sharp molecular mass ions with the maximum mass at m/z 2136 (MH⁺) (Figure 2c). It was accompanied by a relatively simple spectrum showing fully fragmented mass ions at m/z 763, 735, and 720 corresponding clearly to the mass of C₆₀[(C=O)-H]⁺, C₆₀>H⁺, C₆₀⁺, respectively, that is consistent well with the molecular structure of triad **3**. In the case of tetrad **4**, a group of sharp molecular mass ions with the maximum mass at m/z 2673 (MH⁺) and similar fragmented mass ions to those of **3** in the low mass region of m/z 720–1000 were detected (Figure 2d). These MS data revealed high stability of aromatic diphenylaminofluorene moiety under measurement conditions. Additional high mass groups of peaks with the peak maximum at m/z 2160 of Figure 2c and m/z 2696 of Figure 2d are satellite peaks with an increase of 2C (m/z 24) mass from those of molecular ion mass peaks, as common phenomena for fullerenyl nanocarbon materials, especially, under the high laser power conditions used for the collection

of high mass ions. The fragmentation pattern fits well with the bond cleavage occurring mostly at the cyclopropanyl carbon bonds bridging the C_{60} cage and DPAF- C_{18} /CPAF- C_{2M} antenna moiety. The overall spectra provided strong evidence for the mass composition of **3** and **4**.

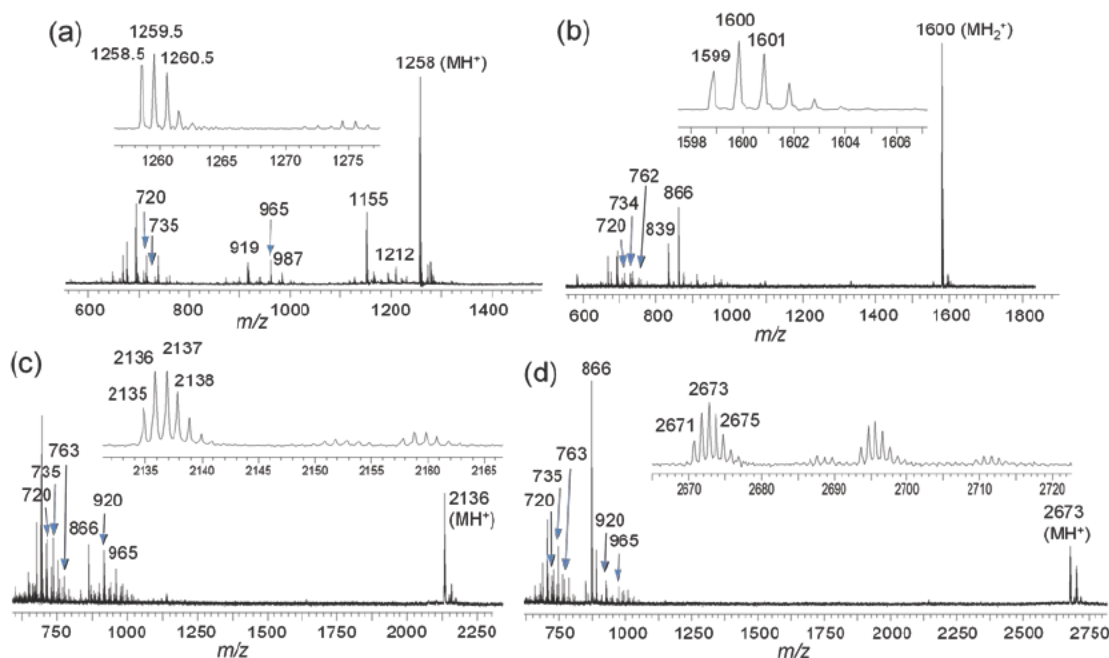


Figure 2. MALDI-TOF mass spectra of (a) C_{60} (>CPAF- C_{2M}) **2**, (b) C_{60} (>DPAF- C_{18}) **1**, (c) C_{60} (>DPAF- C_{18})(>CPAF- C_{2M}) **3** and (d) C_{60} (>DPAF- C_{18})(>CPAF- C_{2M})₂ **4**.

3.3 Linear Optical Properties of Hybrid [60]Fullerene Triads and Tetrads

In UV-vis spectroscopic measurements, optical absorption of monoadducts **1** and **2** (Figures 3a and 3b, respectively) was characterized by two distinguishable bands centered at 260 and 325–327 nm both arising from the C_{60} > cage moiety that agrees with allowed $^1T_{1u} \rightarrow ^1A_g$ transition bands of pristine C_{60} [16]. The third band with λ_{max} at either 411 or 501 nm for **1** or **2**, respectively, matches approximately with those of the corresponding precursor compound BrDPAF- C_{18} , or BrCPAF- C_{2M} . These bands are in the characteristic photoresponsive wavelength range of DPAF- C_{18} or CPAF- C_{2M} .

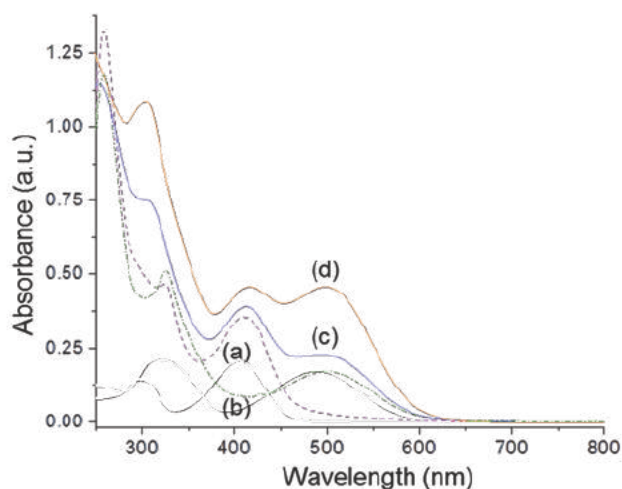


Figure 3. UV-vis spectra of (a) C_{60} (>DPAF- C_{18}) **1**, (b) C_{60} (>CPAF- C_{2M}) **2**, (c) C_{60} (>DPAF- C_{18})(>CPAF- C_{2M}) **3**, and (d) C_{60} (>DPAF- C_{18})(>CPAF- C_{2M})₂ **4** in chloroform at a concentration of 1.0×10^{-5} M.

antenna, respectively. When these two types of antenna were simultaneously attached to the same C_{60} in **3**, two absorption bands with λ_{\max} (ϵ) at 413 (3.9×10^4) and 494 nm (2.3×10^4 L/mol-cm) were observed in the spectrum showing extinction coefficient ϵ values matching roughly with those of **1** and **2**. This clearly revealed a 1:1 ratio of DPAF- C_{18} /CPAF- C_{2M} in **3** consistent with its composition. As the number of CPAF- C_{2M} antenna being increased to two in **4**, the corresponding two bands remained in the same range with λ_{\max} (ϵ) at 417 (4.6×10^4) and 500 nm (4.6×10^4 L/mol-cm). The extinction coefficient (ϵ) value of the second band is nearly double to that of **3**. The structural modification resulted in approximately equal visible absorption in intensity over the full wavelength range of 400–550 nm. Accordingly, these bands can be utilized for the corresponding near-IR two-photon absorption excitation at 800–1100 nm, giving broadband characteristics of the materials while exhibiting good linear transparency beyond 800 nm.

3.4 Two-photon Absorption (2PA) Measurements via Z-scans and Light-intensity-dependent Transmittance

Femtosecond Z-scans and nonlinear light-intensity transmittance reduction measurements of hybrid triad **3** and tetrad **4** were performed as a function of irradiance intensity using 125-fs laser pulses at either 780 nm (corresponding to the two-photon absorption of DPAF moieties) or 980 nm (corresponding to the two-photon absorption of CPAF moieties) at the concentration of 5×10^{-3} M in toluene. These different near-IR wavelength ranges were used to demonstrate the broadband nonlinear photoresponsive ability of the corresponding hybrid C_{60} -(antenna)₂₋₃ analogous. All data were summarized in Figure 4. Simultaneous 2PA cross-section (σ_2) values were calculated from femtosecond Z-scan data and the coefficient by the formula $\sigma_2 = \beta \hbar \omega / N$ with the method for data reduction and line fitting described in the experimental section. For the comparison and discussion purpose, measurements and the σ_2 values of C_{60} (>CPAF- C_9) and C_{60} (>DPAF- C_9) were also performed to demonstrate the strong concentration-dependent σ_2 values through solution concentration between 10^{-3} – 10^{-2} M owing to the aggregation effect. Only a moderate σ_2 value of 46 GM was measured at the concentration of 1.0×10^{-2} M. A 5–6 folds increase of the σ_2 value to 275 GM was achieved by simply decreasing the concentration to 1.0×10^{-3} M. The phenomena were much more pronounced for the dyad C_{60} (>DPAF- C_9) when the irradiation wavelength of 780 nm matched with two-photon absorption of DPAF- C_9 antenna. In this case, a 70-fold increase in the σ_2 value to 2190 GM was measured at 1.0×10^{-4} M, as compared with a 30 GM value at 1.0×10^{-2} M [15]. Since the 2PA measurement was performed at the focal area of the laser pulse, the signal intensity could be as low at 10^{-4} M leading to less accuracy in the calculation and line-fitting of the Z-scan data. Therefore, we used a medium concentration of 2.0 – 5.0×10^{-3} M for this study. It is interesting to note that, even though the irradiation wavelength of 780 nm was not the best fit to the 2PA absorption λ_{\max} of C_{60} (>CPAF- C_9) at 1000 nm, we still observed appreciable cross-section values. This could be owing to C_{60} -(antenna)_x nanostructures in general acting as broadband NLO materials since the optical absorption of the chromophore component covers a broad wavelength range. In the comparison between hybrid triads **3** and **3**- C_9 , C_{60} (>DPAF- C_9)(>CPAF- C_{2M}), we noticed that the use of long *n*-octadecyl chains (C_{18}) in **3** increased the solubility of nanostructure in toluene, as compared with that of the branched 3,5,5-trimethylhexyl (C_9) groups in **3**- C_9 , and was able to produce a slightly higher 2PA σ_2 value of 221 GM, even though the measurement was made by a solution with 3 times higher in concentration. This value is much lower than that of C_{60} (>DPAF- C_9) in CS_2 . Apparently, the solvent effect arising from CS_2 may play a significant role in the value of σ_2 . For the hybrid tetrad **4**, the σ_2 value of 266 GM was slightly higher than that of **3** since the number of photoresponsive DPAF- C_{18} antenna was the same for both structures. An additional CPAF- C_{2M} antenna in **4** increased its σ_2 value by 45 GM. The second set of Z-scan experiments were performed in toluene using a pulse laser with a 125-fs pulse duration width at 980 nm to match with the linear absorption λ_{\max} of the CPAF- C_{2M} antenna at 500 nm. As expected, the 2PA cross-section values of C_{60} (>DPAF- C_9) as 85 ($I = 48$) and 130 ($I = 104$ GM/cm²) GM (Table 3) were found to be moderate at the concentration of 5.0×10^{-3} M since the 2PA energy at 980 nm is less than the main linear absorption λ_{\max} (408 nm) of the DPAF- C_9 antenna. Higher 2PA σ_2 values of 450 ($I = 48$) and 538 ($I = 104$ GM/cm²) GM for C_{60} (>CPAF- C_9) were measured in similar experiments, consistent with using well-matched absorption and excitation wavelengths. With an additional DPAF- C_{18} arm attached to the structure of **3**, no increase of σ_2 values was found with $\sigma_2 = 504$ GM ($I = 104$ GM/cm²) in the same range as that of C_{60} (>CPAF- C_9). As the number of 980-nm-responsive antenna was increased to two in the structure of hybrid tetrad **4**, C_{60} (>DPAF- C_{18})(>CPAF- C_{2M})₂, the σ_2 values were doubled to 995 ($I = 48$) and 1100 ($I = 104$ GM/cm²) GM. These data further demonstrated the suitability of **3** and **4** to be used as broadband NLO materials at 780–1000 nm [17].

Nonlinear light-transmittance measurements of C_{60} (>CPAF- C_9), **3**, and **4** were performed as a function of irradiance intensity with 125-fs laser pulses at either 800 or 980 nm with the concentration of 5×10^{-3} M in toluene. As shown in Figure 4, the Z-scans displayed positive signs for absorption nonlinearities with a decreasing trend of light-transmittance (Figure 4c, 980 nm) in the order of **4** > **3** \approx C_{60} (>CPAF- C_9) in solution with the input intensity of 104 GW/cm². The plot of transmittance (%) vs irradiance (GW/cm²) of all samples showed a linear transmission ($T = \sim 95\%$)

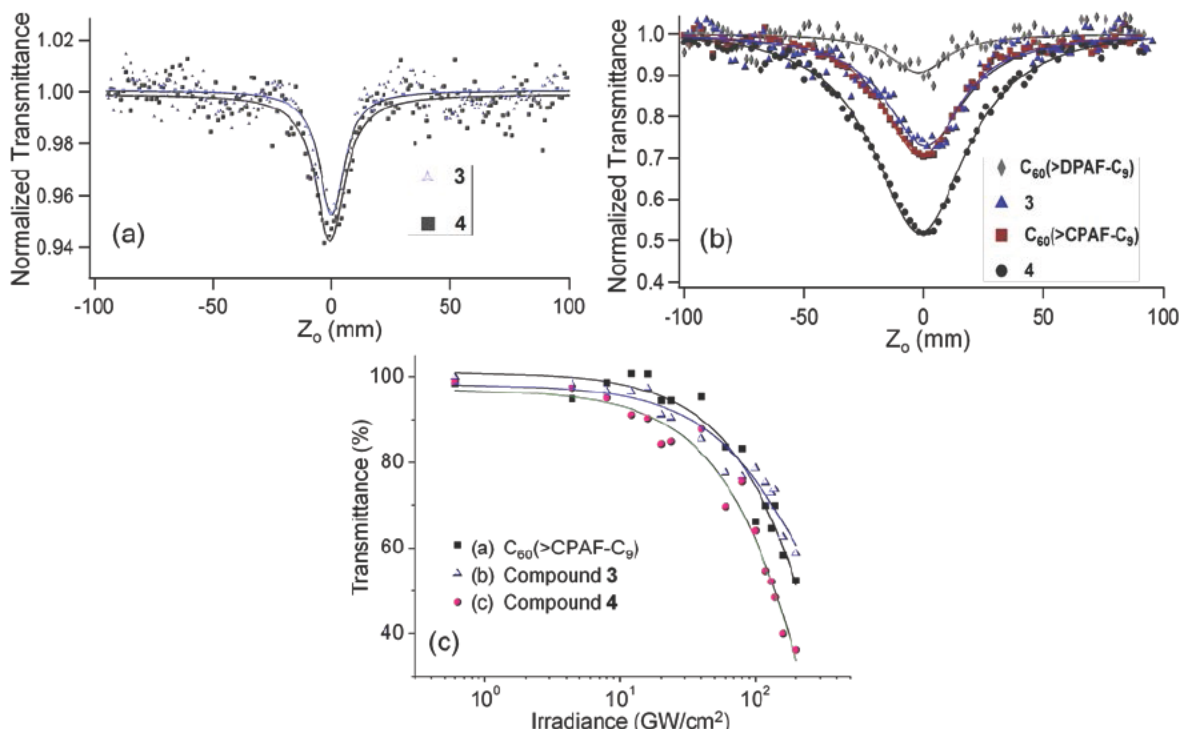


Figure 4. Open-aperture Z-scan profiles of (a) $C_{60}(>DPAF-C_{18})(>CPAF-C_{2M})_2$ **3** and $C_{60}(>DPAF-C_{18})(>CPAF-C_{2M})_2$ **4** using 125 fs laser pulses operated at 800 nm and the input intensity of 270 GW/cm², (b) $C_{60}(>DPAF-C_9)$, $C_{60}(>CPAF-C_9)$, **3**, and **4** using 125-fs laser pulses operated at 980 nm and the input intensity of 104 GW/cm², and (c) nonlinear transmittance of $C_{60}(>CPAF-C_9)$, **3**, and **4** as a function of light intensity carried out with 125-fs laser pulses operated at 980 nm. All measurements were carried out at the concentration of 5×10^{-3} M in toluene.

with input intensity of up to 20 GW/cm². When the incident light intensity was increased above 30 GW/cm², the transmittance (%) began to deviate from the linear transmission line and decrease indicating the initiation of nonlinearity and the transmittance reduction effect. The transmitted fluence further departed from the linear line upon the increase in the incident fluence. A trend showing higher efficiency in reducing light-transmittance down to 50, 55, and 35% for $C_{60}(>CPAF-C_9)$, **3**, and **4**, respectively, was observed with the increase of light intensity up to 110 GW/cm². The observed improvement in lowering the transmitted light-intensity by **4** is consistent with its better nonlinear contribution that can be correlated to its higher fs 2PA cross-sections, as shown by the Z-scans.

4. CONCLUSIONS

Two new $C_{60}-(antenna)_x$ analogous nanostructures with the covalent attachment of multiple antenna units were synthesized and characterized by various spectroscopic methods. Structural design of these nanomaterials was intended to facilitate the ultrafast femtosecond intramolecular energy-transfer process from the photoexcited $C_{60}[>^1(DPAF)^*-C_{18}](>CPAF-C_{2M})_{1or2}$ or $C_{60}(>DPAF-C_{18})[>^1(CPAF)^*-C_{2M}]_{1or2}$ to the C_{60} cage moiety upon two-photon pumping at either 780 or 980 nm, respectively. By adjustment of a higher number of CPAF- C_{2M} antenna, the resulting tetrads showed nearly equal absorption in extinction coefficients over the wavelength range of 400–550 nm that corresponds to near-IR two-photon based excitation wavelengths at 780–1100 nm for broadband NLO studies. Aside from their enhanced 2PA activity at 780 nm, we demonstrated the ability of $C_{60}-(antenna)_x$ analogous nanostructures to exhibit ultrafast photo-responses at 980 nm showing 2PA cross-section (σ_2) values of 995–1100 GM for the tetrad. These σ_2 values were correlated to the observed good efficiency in reducing fs light-transmittance down to 35% at the light intensity of 110 GW/cm². The observation also demonstrated the intramolecular/intramolecular interaction between the excited CPAF- C_n donor antenna moiety and the acceptor C_{60} cage that was also confirmed by transient absorption spectroscopic

measurements using ns laser pulses at 480–500 nm [18]. The behavior resembles that of DPAF- C_n antenna with transient photoexcitation at 380–410 nm reported previously [19].

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